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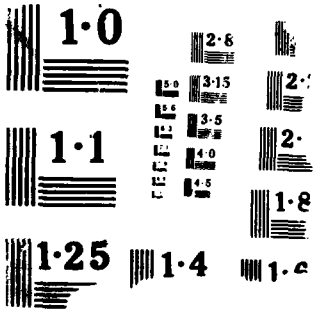
1·0
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POLYFUNCTIONALISATION OF CAGE HYDROCARBONS

Second Interim Report

by

Prof. Dr. Paul von Rague Schleyer

March 1988

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European Research Office of the U.S. Army
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INTRODUCTION.

This report outlines the work being carried at the University of Erlangen-Nurnberg aimed at the synthesis of polyhalogenated cage molecules, their isolation, characterisation, and assessment as potential pre-cursors to "high density" materials.

The progress in this field up to 31/3/88 is reported herein and intended future work is described.

The "cage" systems studied are adamantane($C_{10}H_{16}$), diamantane ($C_{14}H_{20}$), and norbornadiene-dimer($C_{14}H_{16}$) (NBD).

CONTENTS.

(I) Bromination of $AdBr_4$.

A variety of different methods have been employed all without success, the $AdBr_4$ remaining unreacted. The methods attempted are shown in the scheme below.

(1a) $AdBr_4 + Br_2 + CCl_4$ -----hν RT-------> no reaction

(1b) As above + $N{=}NC(CH_3)_2CN$ ---hν RT-------> no reaction

(2) $AdBr_4 + Br_2$ ----hν---------------> no reaction

(3) $AdBr_4$ + NBS + dibenzoylperoxide -----heat--> no reaction

(4) $AdBr_4 + Br_2$ + HgO ----CCl_4 heat ---> no reaction

(5) $AdBr_4 + Br_2$ + HgO ---$BrCl_3C$--hν-> no reaction

(II) Photochlorination of $AdBr_4$.

On short term photochlorination, typically 30-60 mins., a total halogen content of 8 or 9 is achieved.

(1) $AdBr_4$ ------Cl_2-- hν----> $AdBr_4Cl_4 + AdBr_4Cl_5$

On longer photolysis, up to 3 days, a higher halogen content is obtained. This product is not yet fully analysed but from ^1H NMR is estimated to contain a total halogen content of around 12.

(2) $AdBr_4$ --------Cl_2-- hν-> $AdBr_4Cl_7$
^1H nmr(m,4.0, m,6.1ppm)

(III) Photochlorination of Adamantane.

20hrs. photochlorination results, after work up, in a product mixture of the following composition:

$C_{10}Cl_{12}H_4$ 68%, $C_{10}Cl_{13}H_3$ 29%, $C_{10}Cl_{14}H_2$ 3%.

This composition is calculated by comparing the peak intensities for the $(M-Cl)^+$ ions. (The $M^{+\cdot}$ peaks are very weak for these compounds). The mixture exhibits the ^1H nmr spectrum; (m,3.65, m,6.0ppm)

Chlorination of Tetrachloroadamantane $AdCl_4$.

Short term photolysis results in the formation of $AdCl_5$ and $AdCl_6$ which together exhibit the ^1H nmr spectrum (m,3.3, m,5.2ppm).

Photolysis for 52hrs results in further chlorination , the product found by mass spec. to be a mixture of Cl_{11},Cl_{12},Cl_{13} and Cl_{14} compounds. This mixture exhibits the ^1H nmr spectrum (m,3.6 CH_2, m,5.8 CHCl).

Partial evaporation of a solution of this mixture in Et_2O results in crystallisation. X-Ray analysis of these crystals reveals that they belong to the Cubic system but also that they are severely disordered indicating the probability that the very similar packing properties of the Cl_{11}-Cl_{14} compounds allow them to crystallise together. Further X-Ray analysis on these crystals was therefore impossible due to the disorder. Mass spec. analysis of these crystals indicates the following approximate composition:

$AdCl_{12}H_4$ 49%, $AdCl_{13}H_3$ 38%, $AdCl_{14}H_2$ 13%.

The 400MHz ^1H nmr spectrum is provided (spec.1)

HPLC separation of this crystalline mixture using petrolether/Et_2O 95:5 %vol gives two distinct fractions(1 and 3) which were at first thought to be only mixtures enriched in one or other chloroadamantane. It now seems more probable that the two fractions, although exhibiting similar mixture compositions, in fact contain distinct isomers of these components.

The compositions of the fractions, estimated by comparison of the intensities of the $(M-Cl)^+$ peaks in the mass spectra, are as follows;

FRACTION 1	COMPOUND	FRACTION 3
39%	AdH_4Cl_{12}	46%
35%	AdH_3Cl_{13}	54%
26%	AdH_2Cl_{14}	--

In both fractions, the compounds of molecular formula AdH_4Cl_{12} and AdH_3Cl_{13} are major components and present in fairly equal amounts. The 400MHz ^1H nmr spectra of these two fractions are, however, very different. Spectra provided (spec.2 and spec.3).

The spectrum for fraction 1 (spec.2) exhibits many resonances in the region which corresponds to the R_2CHCl function (~6.0ppm) and also a few less intense peaks in the R_2CH_2 region.

All of these peaks are absent from the spectrum of fraction 3 (spec.3). An explanation of this is that fraction 1 contains mainly those isomers of the Cl_{12},Cl_{13} and Cl_{14} compounds which contain no R_2CH_2 groups. This is consistant with the fact that these isomers have inherently lower dipoles than those not containing such groups, and therefore would be eluted first in the HPLC by the non-polar solvent.

As mentioned, only fraction 1 contains the $AdCl_{14}H_2$ isomers all of which probably contain no R_2CH_2 groups. Fraction 3, on the other hand, contains those isomers of $AdCl_{12}H_4$ and $AdCl_{13}H_3$ which do contain a R_2CH_2 group. These have fewer isomeric possibilities. This fact and the absence of $AdCl_{14}H_2$ combine to greatly simplify the nmr spectrum (spec.3).

Semi empirical molecular mechanics (MNDO) calculations on the isomers of $AdCl_{12}H_4$ containing no R_2CH_2 groups show the following;

ISOMER	RELATIVE ENERGY Kcal/Mol.
C_s	0.0
S_4	1.0
C_{2v}	1.9
all C_1	>6.8

These results clearly show that the C_1 isomers are energetically disfavoured and this agrees with both the ^1H and ^{13}C spectra (spec.2 & 4) which do not contain enough peaks for the C_1 isomers to be accounted for.

The C_s, S_4, and C_{2v} isomers could conceivably all be produced although in differing amounts. This also agrees with the spectral data.

More detailed calculations on these isomers and on those containing R_2CH_2 groups could help identify those isomers formed in preference, which can only be decided unambiguously by X-Ray analysis, which, as mentioned earlier, poses problems in crystal growth due to the similarity in the packing characteristics of these spherically shaped molecules.

(IV)Chlorination of diamantane.

Ionic chlorination of diamantane using $AlCl_3$ results in the formation of $C_{14}H_{16}Cl_4$ which is highly insoluble in anything except THF.

Photochlorination of diamantane, for approximately 24hrs results in a mixture of the following estimated composition (mass spec.).

$C_{14}H_{10}Cl_{10}$ 45%, $C_{14}H_9Cl_{11}$ 45%, $C_{14}H_8Cl_{12}$ 9%, $C_{14}H_7Cl_{13}$ 1%.

(V) Chlorination of norbornadiene dimer (NBD) ($C_{14}H_{16}$)

Ionic chlorination of NBD results in products in the Cl_4-Cl_7 range. The composition estimated from the mass spectrum is as follows;

$C_{14}H_{12}Cl_4$ 35%, $C_{14}H_{11}Cl_5$ 56%, $C_{14}H_{10}Cl_6$ 9%.

Photochlorination of NBD, proceeds somewhat further yielding compounds in the Cl_8-Cl_{10} range.Composition estimate from mass spec. is as follows;

$C_{14}H_8Cl_8$ 6.5%, $C_{14}H_7Cl_9$ 81%, $C_{14}H_6Cl_{10}$ 12.5%.

The Cl_9 compound precipitates from the reaction. The Cl_8 compound can be obtained in 92% purity by filtering off the Cl_9 compound and working up.

(VI) Bromination of diamantane.

A selective method for the synthesis of 4,9-dibromodiamantane from diamantane in 85% yield has been developed.

$C_{14}H_{20} + Br_2 + Fe$ ---RT 2hrs------> $C_{14}H_{18}Br_2$

This compound may prove to be a more suitable starting point than tetrabromodiamantane, for further halogenation, due to its higher solubility in the solvents usually employed in photohalogenations.

(x) Conclusions and intended future work.

Chlorination of adamantane has now succeeded in producing major products in the Cl_{12}-Cl_{14} range which corresponds to over 75% functionalisation.

Partial separation of the isomers produced has been achieved by HPLC in quantities which allow analysis by 400MHz ^1H nmr.

It has not yet been possible to separate the Cl_{12} and Cl_{13} compounds by this method but separation of the isomers of these compounds which contain unfunctionalised R_2CH_2 groups from those which do not, has been achieved. Further identification requires larger quantities of separated isomers for ^{13}C and ^{13}C-^1H shift correllated spectroscopy.

Reversed phase HPLC could be useful in separating $AdCl_{12}$ and $AdCl_{13}$ from pre-separated R_2CH_2 containing,and non-containing isomer mixtures.

Further MNDO calculations on the various isomers of $AdCl_{12}$, $AdCl_{13}$, and $AdCl_{14}$ will aid identification of preferentially formed isomers. The growth of crystals suitable for X-Ray analysis is being actively pursued.

Photochlorination of $AdCl_4$ also proceeds to the Cl_{12}-Cl_{14} range. It is not yet clear whether the isomeric distribution here is the same as it is in the case of directly photochlorinated adamantane. Again samples are being purified for ^{13}C and ^{13}C-^1H correllated nmr spectroscopy.

Photobromination has been somewhat less successful, with the attempted bromination of pre-halogenated adamantanes not proceeding at all, and that of adamantane only to the Br_3-Br_5 range.

Chlorination of other cage systems, diamantane, and NBD has also proceeded well, products in the Cl_{12}-Cl_{14} and Cl_7-Cl_9 ranges being produced respectively. This corresponds to 70% and 50% functionalisation.

Photochlorination of ionically brominated cages has begun with initial experiments yielding $AdBr_4Cl_4$-$AdBr_4Cl_6$ compounds which appear to be more amenable as far as crystallisation is concerned.

Two computer programs have been written which significantly simplify the interpretation of the mass spectra of these highly halogenated and mixed halogen compounds.

Methods of halogen exchange (from Cl or Br to I) are being investigated with some success.

Scientific personnel involved in this work:

Prof. Dr. P.v.R. Schleyer (Principal Investigator)

Dr. Peter Gregory (post doctoral associate)

Erlangen, April 6, 1988

POLYCHLOROADAMANTANE [illegible]

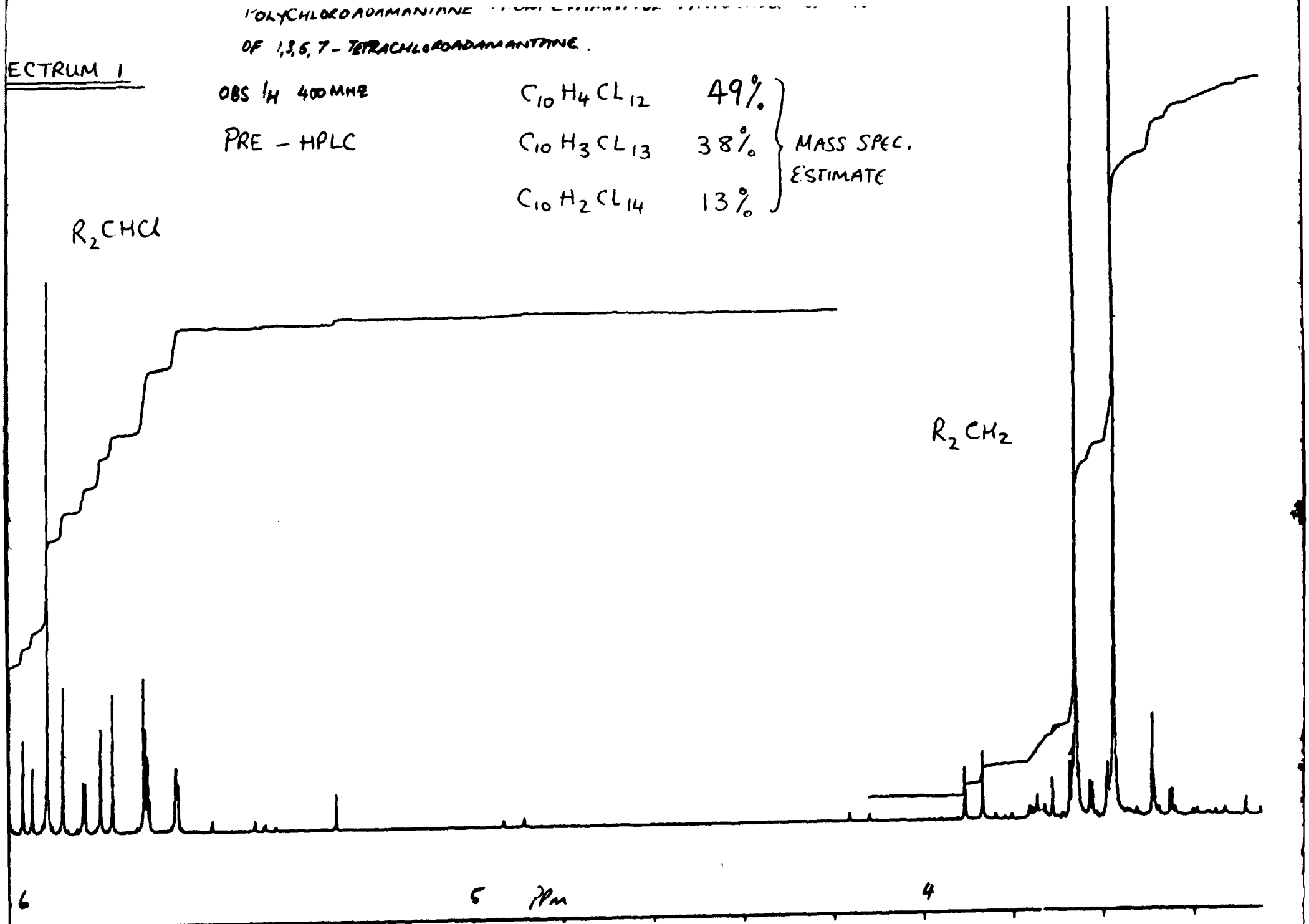
OF 1,3,6,7-TETRACHLOROADAMANTANE.

ECTRUM 1

OBS ^1H 400 MHz

PRE – HPLC

$C_{10}H_4Cl_{12}$	49%	} MASS SPEC. ESTIMATE
$C_{10}H_3Cl_{13}$	38%	
$C_{10}H_2Cl_{14}$	13%	



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ABOBS 399726.8000000 KHZ
NGAIN 15
COMNT 85095/P.GREGORY/CL-ADAMANTANE/CDCL3/1H/HS/+26DEG

NO.	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	7.52210	0.07589	3007.20	5893	
2	7.26332	6.64536	2903.75	6232	* $CHCl_3$
3	6.28699	0.18926	2513.63	7511	
4	6.22668	0.07961	2489.52	7590	
5	6.21523	0.23879	2484.76	7605	
6	6.16867	1.07743	2466.13	7666	
7	6.13584	0.15178	2453.00	7709	
8	6.11600	0.24379	2445.07	7735	
9	6.10378	0.07267	2440.19	7751	
10	6.09386	0.09826	2436.22	7764	
11	6.08775	0.09212	2433.78	7772	
12	6.05569	0.11009	2420.96	7814	
13	6.04500	0.71671	2416.69	7828	
14	6.04195	0.22613	2415.47	7832	
15	6.03050	7.66135	2410.89	7847	** R_2CHCl
16	6.02363	0.21196	2408.14	7856	
17	6.01905	0.12724	2406.31	7862	
18	6.01371	0.08162	2404.17	7869	
19	5.99539	1.50144	2396.85	7893	
20	5.97401	1.07675	2388.31	7921	
21	5.95188	0.18569	2379.46	7950	
22	5.94063	8.83768	2376.88	7965	**
23	5.92898	0.15134	2370.30	7980	
24	5.90684	2.32709	2361.45	8009	
25	5.87325	0.11562	2343.02	8053	
26	5.86256	0.84685	2343.75	8067	
27	5.85722	0.83090	2341.61	8074	
28	5.82287	1.66055	2327.88	8119	
29	5.80836	0.07892	2322.08	8138	
30	5.79615	2.21793	2317.20	8154	
31	5.73966	0.10553	2294.62	8228	
32	5.72745	2.46002	2289.73	8244	
33	5.72287	1.65931	2287.90	8250	
34	5.71905	1.22502	2286.38	8255	
35	5.71447	0.50939	2284.55	8261	
36	5.65722	1.03668	2261.66	8336	
37	5.65340	0.64309	2260.13	8341	
38	5.65188	0.79604	2259.52	8343	
39	5.64348	0.08886	2256.16	8354	
40	5.57707	0.18735	2229.61	8441	
41	5.48241	0.17256	2191.77	8565	
42	5.46180	0.09908	2183.53	8592	
43	5.45951	0.12049	2182.62	8595	
44	5.43585	0.07760	2173.16	8626	
45	5.30150	0.58185	2119.45	8802	
46	4.93051	0.12530	1971.13	9288	
47	4.88547	0.15218	1953.13	9367	
48	4.16486	0.15609	1665.04	10291	
49	4.11982	0.12806	1647.03	10350	
50	3.90609	0.85329	1561.58	10630	
51	3.86715	1.09685	1546.02	10681	
52	3.83891	0.11375	1534.73	10718	
53	3.80227	0.10272	1520.08	10766	
54	3.76181	0.20836	1503.91	10819	
55	3.75952	0.14256	1502.99	10822	
56	3.75494	0.19437	1501.16	10828	
57	3.75112	0.14359	1499.63	10833	
58	3.74502	0.38807	1497.19	10841	
59	3.73891	0.15056	1496.75	10849	
60	3.72822	0.23019	1490.48	10863	
61	3.71067	0.65117	1483.46	10886	
62	3.68853	0.10376	1474.61	10915	
63	3.68242	0.08788	1472.17	10923	
64	3.67174	0.92214	1467.90	10937	
65	3.66563	1.33818	1465.45	10945	
66	3.65952	15.65355	1463.01	10953	*** R_2CH_2
67	3.65189	0.86309	1459.96	10963	
68	3.62746	0.60119	1450.20	10995	
69	3.62135	0.56634	1447.75	11003	
70	3.61143	0.10793	1443.79	11016	
71	3.59158	0.94759	1435.85	11042	
72	3.58929	0.90133	1434.96	11045	
73	3.58700	0.65789	1434.02	11048	
74	3.57555	16.54562	1429.44	11063	***
75	3.56868	0.93355	1426.70	11072	
76	3.54426	0.14219	1418.93	11104	
77	3.53891	0.12695	1416.79	11111	
78	3.52288	0.16527	1408.39	11132	
79	3.51754	0.08055	1406.25	11139	
80	3.49006	1.63376	1395.26	11175	
81	3.48471	0.68254	1393.13	11182	
82	3.47555	0.17007	1389.47	11194	
83	3.45189	0.43288	1380.00	11225	
84	3.44685	0.46387	1377.87	11232	
85	3.44044	0.16864	1375.43	11240	
86	3.40181	0.13010	1359.86	11291	
87	3.39235	0.14425	1356.20	11303	
88	3.36868	0.09383	1346.74	11336	
89	3.36478	0.09697	1345.83	11339	

FRACTION 1 FROM HPLC OF PGA8/10. PETROLETHER/DIETHYLETHER 95:5 VOL.

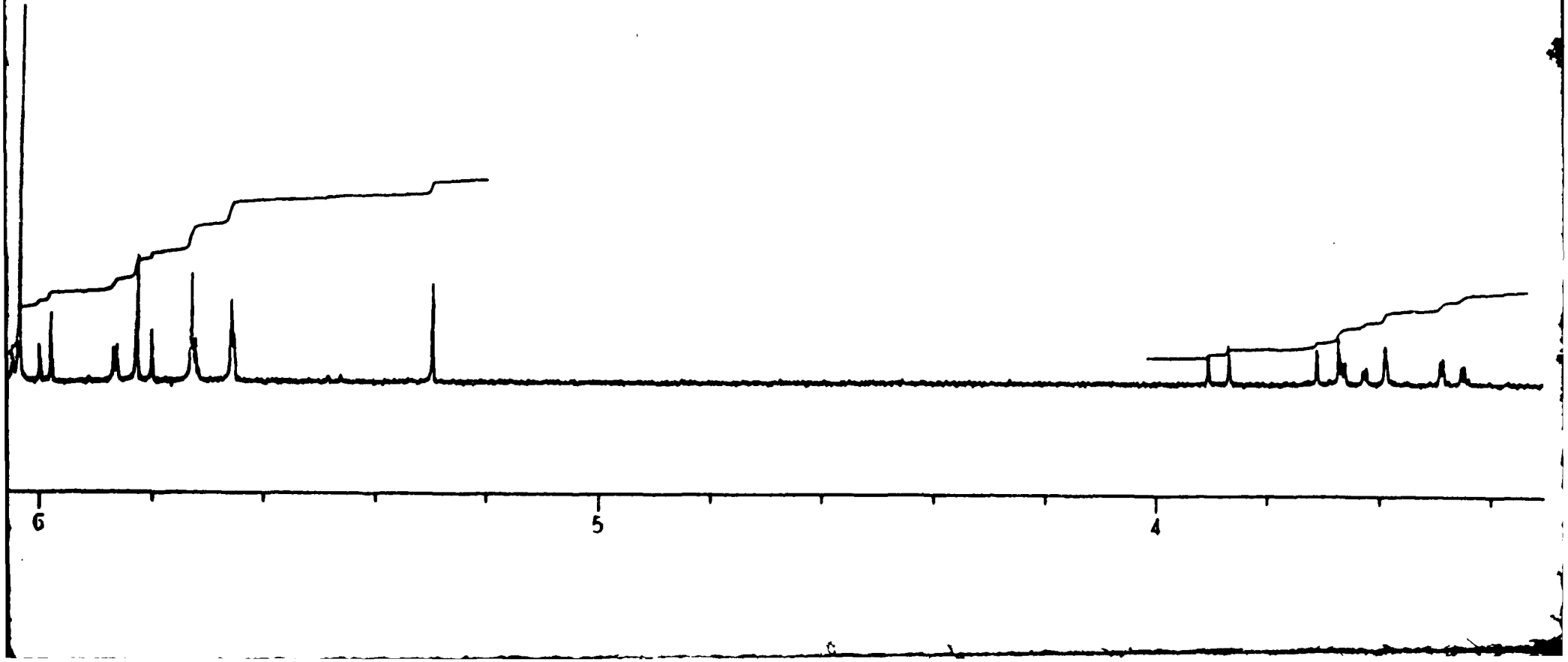
OBS ^1H 400 MHZ

SPECTRUM 2

$C_{10}H_4Cl_{12}$ 39%
$C_{10}H_3Cl_{13}$ 35%
$C_{10}H_2Cl_{14}$ 26%
} MASS SPEC ESTIMATE.

R_2CHCl

R_2CH_2



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1	7.26561	5.49368	2904.66	6231	+ $CHCl_3$
2	6.17630	0.66949	2469.18	7658	
3	6.05111	0.68401	2419.13	7822	
4	6.03813	6.27609	2413.94	7839	+ R_2CHCl
5	6.00226	0.69371	2399.60	7886	
6	5.98165	1.22259	2391.36	7913	
7	5.87020	0.65814	2346.80	8059	
8	5.86409	0.69479	2344.36	8067	
9	5.82898	2.15283	2330.32	8113	
10	5.80302	0.94313	2319.95	8147	
11	5.73432	1.85953	2292.48	8237	
12	5.72669	0.79241	2289.43	8247	
13	5.66333	1.43001	2264.10	8330	
14	5.65875	0.89304	2262.27	8336	
15	5.30302	1.71058	2120.06	8802	
16	3.90990	0.57573	1563.11	10627	
17	3.87173	0.73602	1547.85	10677	
18	3.71372	0.65704	1484.68	10884	
19	3.67555	0.85458	1469.42	10934	
20	3.67097	0.46937	1467.59	10940	
21	3.66487	0.45714	1465.15	10948	
22	3.59235	0.72266	1436.16	11043	
23	3.49464	0.47613	1397.09	11171	R_2CH_2
24	3.48929	0.51757	1394.96	11178	
;	2.34045	0.55242	935.67	12683	
26	2.33052	0.53226	931.70	12696	
27	2.21449	0.96716	885.31	12848	
28	2.17403	100.00000	869.14	12901	++++++++++++++++++
29	2.13129	1.07525	852.05	12957	
30	2.01220	0.43865	804.44	13113	
31	1.59388	1.05014	637.21	13661	
32	0.04046	0.80271	16.17	15696	
33	0.00840	2.99922	3.36	15738	+
34	0.00000	66.66846	0.00	15749	++++++++++++
35	-0.00840	2.66802	-3.36	15760	+
36	-0.04198	0.48176	-16.78	15804	

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PW3 33.0

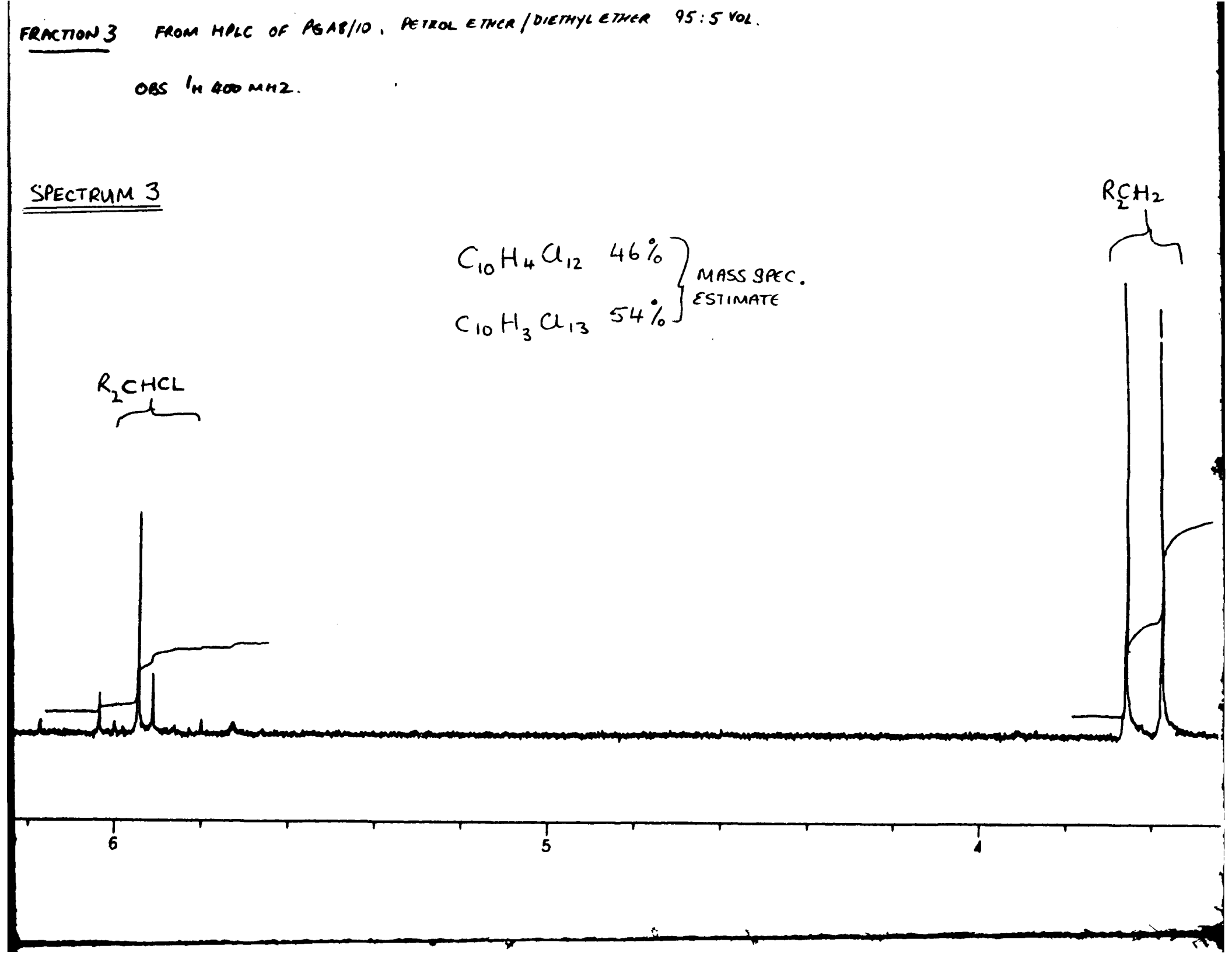
FRACTION 3 FROM HPLC OF PGAB/10. PETROL ETHER / DIETHYL ETHER 95:5 VOL.

OBS ^1H 400 MHZ.

SPECTRUM 3

$C_{10}H_4Cl_{12}$ 46% } MASS SPEC. ESTIMATE

$C_{10}H_3Cl_{13}$ 54% }



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NO.	PPM	INT(%)	FREQ(Hz)	POSITION	BAR GRAPH
1	7.26103	28.23798	2902.83	6230	++++++ $CHCl_3$
2	6.03813	1.36029	2413.94	7832	
3	5.94806	7.04529	2377.93	7950	+ } R_2CHCl
4	5.91523	1.98020	2364.81	7993	
5	3.66410	14.72423	1464.84	10942	+++
6	3.58090	13.83143	1431.58	11051	+++ } R_2CH_2
7	2.70457	2.49464	1081.24	12199	
8	2.17327	0.90036	868.84	12895	-
9	1.54885	3.20507	619.20	13713	+
10	1.53969	1.82560	615.54	13725	
11	1.52213	1.07773	608.52	13748	
12	1.50305	3.15426	600.89	13773	+
13	1.32900	0.85171	531.31	14001	
14	1.30763	1.28600	522.77	14029	
15	1.28931	1.61713	515.44	14053	
16	1.27099	1.83422	508.12	14077	
17	1.25266	1.81832	500.79	14101	
18	1.22137	0.63397	488 28	14142	
19	1.17022	1.03425	467.83	14209	
20	1.15343	1.58423	461.12	14231	
21	1.13129	1.40567	452.27	14260	
22	1.10457	0.71636	441.59	14295	
23	0.89389	3.47061	357.36	14571	+
24	0.88320	2.23065	353.09	14585	
25	0.87557	8.55405	350.04	14595	++ } PETROL ETHER
26	0.87099	13.49026	348.21	14601	+++
27	0.85496	15.06149	341.80	14622	+++ }
28	0.85038	5.16451	339.97	14628	+
29	0.84427	4.46447	337.52	14636	+
30	0.83816	3.86436	335.08	14644	+
31	0.83358	4.44974	333.25	14650	+
32	0.82748	3.87931	330.81	14658	+
33	0.06870	1.10554	27.47	15652	
34	0.03435	1.06598	13.73	15697	
35	0.02214	0.74910	8.85	15713	
36	0.00687	5.44087	2.75	15733	+
37	0.00000	100.00000	0.00	15742	++++++++++++++++++++
38	-0.00840	4.22455	-3.36	15753	+
39	-0.01985	1.91707	-7.93	15768	
40	-0.03511	1.43835	-14.04	15788	

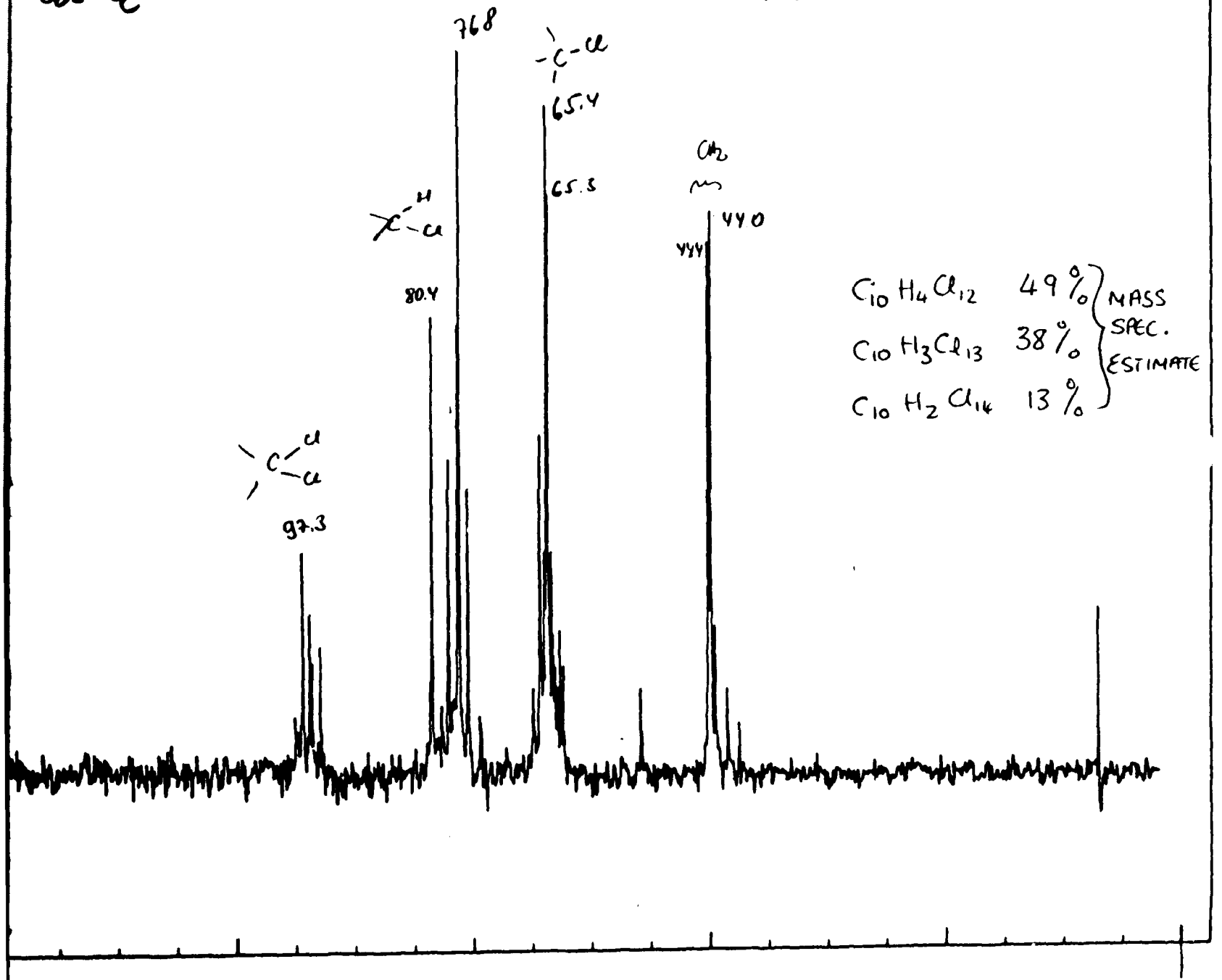
14-DEC-87 12:13:12
OBNUC 1H
OBFRQ 399.65 MHz
OBSET 120.00 kHz
OBFIN 14811.2 Hz
PW1 3.0 us
PW2 33.0 us

POLYCHLORODIAMANTANE

OBS ^{13}C

SPECTRUM 4

PRE - HPLC



$C_{10}H_4Cl_{12}$	49 %	MASS SPEC. ESTIMATE
$C_{10}H_3Cl_{13}$	38 %	
$C_{10}H_2Cl_{14}$	13 %	

NUCLEUS ^{13}C

OBS.

LOCK ( )

IRR.

FREQUENCY

OBS. H

LOCK H

IRR. H

PULSE ☐ SINGLE ☐ MULTI

WIDTH μ SEC. ( )'

INTERVAL SEC.

REPETITION SEC.

DATA POINTS

WINDOW

SWEEP RANGE H

FILTER B.W. H

AMPLITUDE R.F. A.F.

NO. OF SCANS

DECOUPLING ☐ C.W.

☐ NOISE

☐ EXT.

POWER

LOCK LEVEL R.F. A.F.

DATE

OPERATOR

REMARKS

```
ZERO♦      1.3105 SEC  :      6250.00 HZ♦CONST
 C1 =    200 SCANS :
 CQ_? ♦QUIK:5      TYPE        1 :
 R-RATE SIGNAL FILE IS FROM NO.     66 TO NO.     70♦MOVE:70 ♦DISP:H♦MOVE:66 ♦DISP
H♦DISP:H$STOR♦REDUC
FREQ.RANGE=   6250.00 HZ    248.508PPM
RESOLUTION=       0.76 HZ
TOTAL PEAK=     20  NOISE(%)=       2.89  REFERENCE(PPM)=     76.959 : 77

    NO.   POSIT     FREQ(HZ)       PPM    HEIGHT(%)
      1      66    5821.99   231.481   -18.000  ----
      2    4491    2445.98    97.253    16.370  ♦♦♦♦
      3    4520    2423.85    96.374    11.902  ♦♦♦
      4    4530    2416.22    96.068     8.148  ♦♦
      5    4566    2388.76    94.976     9.515  ♦♦
      6    5047    2021.78    80.386    33.223  ♦♦♦♦♦♦♦♦
      7    5117    1968.38    78.265    23.097  ♦♦♦♦♦♦
      8    5159    1936.34    76.991    32.692  ♦♦♦♦♦♦♦♦
      9    5164    1932.52    76.838    52.206  ♦♦♦♦♦♦♦♦♦♦♦♦
     10    5201    1904.29    75.717    20.893  ♦♦♦♦♦
     11    5509    1669.31    66.374    24.751  ♦♦♦♦♦♦
     12    5530    1653.28    65.735    16.224  ♦♦♦♦
     13    5540    1645.66    65.432    48.177  ♦♦♦♦♦♦♦♦♦♦♦♦
     14    5544    1642.60    65.310    41.610  ♦♦♦♦♦♦♦♦♦♦
     15    5559    1631.16    64.857    16.120  ♦♦♦♦
     16    5592    1605.98    63.854    10.486  ♦♦
     17    6235    1115.41    44.350    38.289  ♦♦♦♦♦♦♦♦♦
     18    6246    1107.02    44.015    40.474  ♦♦♦♦♦♦♦♦♦♦
     19    6262    1094.81    43.530    10.687  ♦♦
     20    7932    -179.29    -7.129    11.933  ♦♦♦

                                    ♦DISP:V♦_? ♦MOVE:66 ♦CONST

C1 =    200 SCANS : 2000
C ♦ACCUM CONTINUE
```

$R_2\underline{C}CL_2$

$R_2\underline{C}HCl$

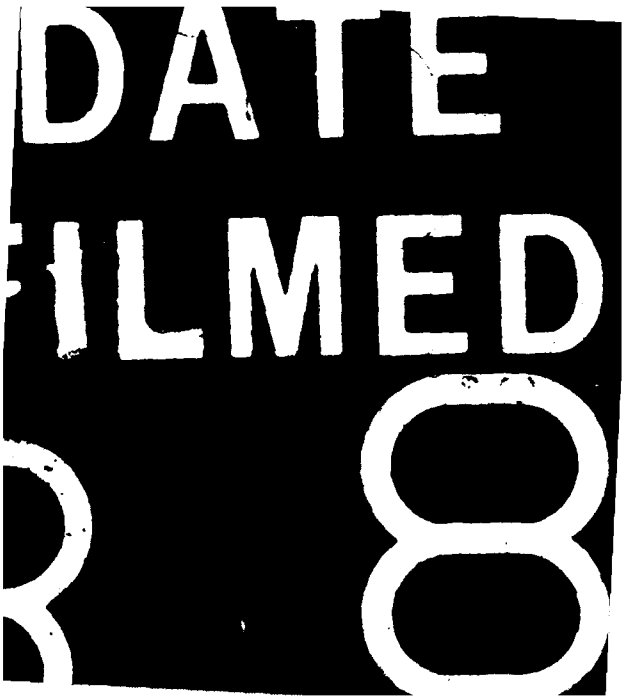
$R_3\underline{C}Cl$ (BRIDGEHEADS)

$R_2\underline{C}H_2$

768

80.4

92.3


DATE
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8